



Crystal structure of 5-amino-4*H*-1,2,4-triazol-1-ium pyrazine-2-carboxylate: an unexpected salt arising from the decarboxylation of both precursors

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Keywords: crystal structure; ionothermal synthesis; decarboxylation; triazolium salt; hydrogen bonding; π - π stacking interactions

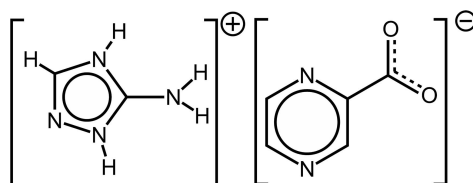
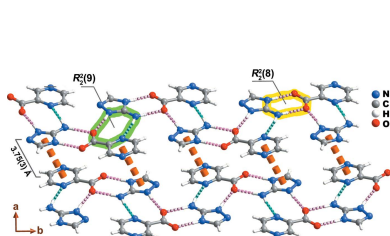
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Both the 3-amino-2*H*,4*H*-1,2,4-triazolium cation and the pyrazine-2-carboxylate anion in the title salt, $C_2H_5N_4^+ \cdot C_5H_3N_2O_2^-$, were formed by an unexpected decarboxylation reaction, from 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid and pyrazine-2,3-dicarboxylic acid, respectively. The dihedral angle between the pyrazine ring (r.m.s. deviation = 0.008 Å) and the carboxylate group in the anion is 3.7 (3)°. The extended structure of the salt contains a supramolecular zigzag tape in which cations and anions are engaged in strong and highly directional N—H...N,O hydrogen bonds, forming $R_2^2(8)$ and $R_2^2(9)$ graph-set motifs. The packing between the tapes is mediated by π - π stacking interactions between the triazole and pyrazine rings.

1. Chemical context

A remarkable feature of ionothermal synthesis is the fact that ionic liquids (ILs) can act simultaneously as sustainable solvents and structure-directing agents (also known as templates). This has been widely demonstrated by their potential in the discovery of unprecedented crystalline materials (Xu *et al.*, 2013). Following our interest in the design and preparation of new types of metal-organic frameworks (MOFs), we have been exploring the use of 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid (H_2atrc) and pyrazine-2,3-dicarboxylic acid (H_2Pzdc) as a double-ligand system in the presence of transition metal centers using ionothermal synthetic conditions. In the presence of $AgNO_3$ the obtained product revealed, however, to be an unexpected organic salt (Bond, 2007) composed of the 3-amino-2*H*,4*H*(+)-1,2,4-triazolium cation and the pyrazine-2-carboxylate anion.



2. Structural commentary

The title compound is a product of decomposition of the H_2atrc and H_2Pzdc organic molecules by way of decarboxylation leading to, respectively, 3-amino-2*H*,4*H*-1,2,4-triazolium

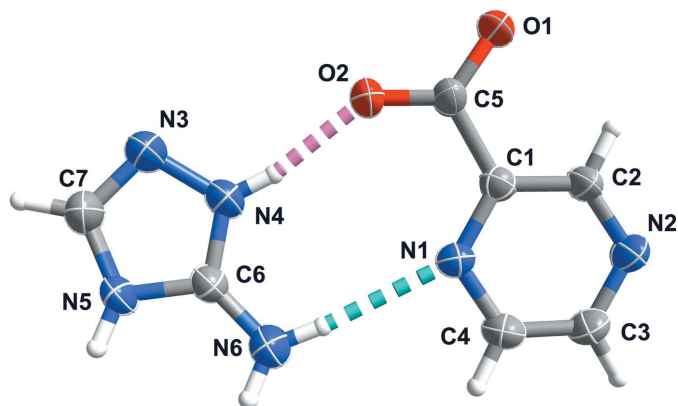


Figure 1

The asymmetric unit of the title salt. Non-H atoms are represented as displacement ellipsoids drawn at the 50% probability level, while H atoms are depicted as small spheres with arbitrary radii. The atomic labelling scheme for all non-H atoms is provided. Hydrogen bonds are represented as dashed lines.

$[(C_2H_5N_4)^+]$ and pyrazine-2-carboxylate $[(C_5H_3N_2O_2)^-]$. The asymmetric unit is composed of one of each of these moieties, as depicted in both the chemical diagram and in Fig. 1.

3. Supramolecular features

The cation present in the title compound is rich in groups capable of forming strong N—H \cdots N/O hydrogen-bonding interactions (see Table 1 for further geometrical details), many highly directional with the observed $\langle D-H\cdots A \rangle$ interaction angles being above 165° . These supramolecular contacts are the main driving force which mediate the crystal packing features of the title compound. Indeed, the donation of hydrogen atoms from the cation to the carboxylate group of an adjacent anion (N6—H6B \cdots O2 and N5—H5 \cdots O1) forms

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4A \cdots O2	0.90 (1)	1.77 (1)	2.655 (3)	166 (3)
N5—H5 \cdots O1 ⁱ	0.90 (1)	1.73 (1)	2.632 (3)	176 (3)
N6—H6B \cdots O2 ⁱ	0.90 (1)	1.97 (1)	2.853 (3)	169 (3)
N6—H6A \cdots N1	0.90 (1)	2.21 (1)	3.099 (3)	169 (3)

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

the known structurally robust $R_2^2(8)$ graph-set motif (dashed pink lines in Fig. 2) (Grell *et al.*, 1999). This graph-set motif has already been found in salts containing the title compound cation and carboxylic acids (see *Database survey* below). Two other interactions, N6—H6A \cdots N1 (dashed aqua lines) and N4—H4A \cdots O2, describe a second $R_2^2(9)$ hydrogen-bond motif. In contrast to the previous graph-set motif, the $R_2^2(9)$ ring has not been observed in structures containing the title-compound cation. The zigzag alternation of these two graph-set motifs leads to the formation of a highly coplanar supramolecular tape running parallel to the [010] direction of the unit cell (Fig. 2). Adjacent tapes interact by way of weak π – π stacking contacts between triazole and pyrazine rings, with the inter-centroid distance being 3.75 (3) \AA (dashed orange lines in Fig. 2).

4. Database survey

Triazole molecules have been extensively used in the preparation of organic co-crystals (Kastelic *et al.*, 2011; Remenar *et al.*, 2003), and a survey of the Cambridge Structural Database (Groom & Allen, 2014) revealed the existence of about a dozen of crystallographic reports of co-crystals of the title compound cation (Byriel *et al.*, 1992; Essid *et al.*, 2013;

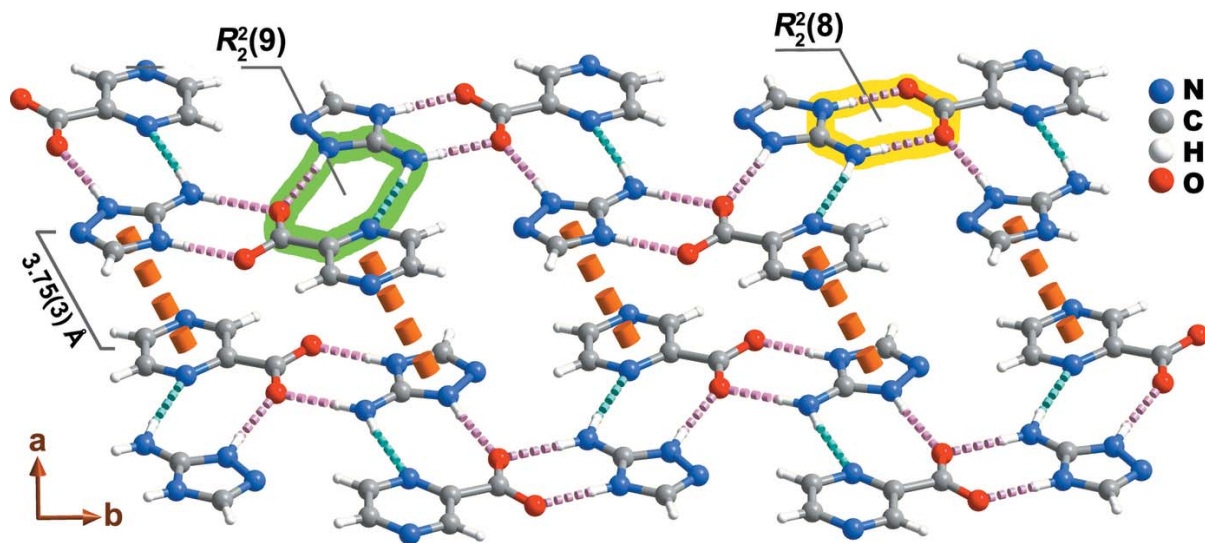


Figure 2

Supramolecular tape running parallel to the [010] direction of the unit cell. N—H \cdots N and N—H \cdots O hydrogen bonds are depicted as dashed aqua and pink lines, respectively. Graph-set motifs present in the structure are highlighted. For geometric details of the represented supramolecular contacts, see Table 1. π – π stacking interactions between two adjacent supramolecular tapes are shown as orange dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_2H_5N_4^+ \cdot C_5H_3N_2O_2^-$
M_r	208.19
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	7.0599 (5), 12.1868 (8), 10.8385 (6)
β (°)	103.593 (4)
V (Å ³)	906.40 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.09 × 0.04 × 0.03
Data collection	
Diffractometer	Bruker X8 Kappa CCD APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1998)
T_{\min} , T_{\max}	0.989, 0.997
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12089, 1858, 1037
R_{int}	0.077
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.133, 1.02
No. of reflections	1858
No. of parameters	148
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.19, -0.20

Computer programs: *APEX2* (Bruker, 2006), *SAINT-Plus* (Bruker, 2005), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2009).

Joo *et al.*, 2013; Luo *et al.*, 2013; Lynch *et al.*, 1992, 1998, 1999; Lynch, Smith, Byriel & Kennard, 1994; Lynch, Smith, Byriel, Kennard *et al.*, 1994; Matulková *et al.*, 2007; Smith *et al.*, 1996). The only compounds known with both of the title compound entities present is a bimetallic complex also containing Cd^{2+} and NO_3^- ions (Chen *et al.*, 2009).

5. Synthesis and crystallization

5-Amino-1*H*-1,2,4-triazole-3-carboxylic acid (H_2atrc , 98% purity), pyrazine-2,3-dicarboxylic acid (H_2Pzdc , 97% purity), 1-methylimidazole (99%+ purity), 1-bromobutane (99% purity) and $AgNO_3$ (99%+ purity) were purchased from Sigma–Aldrich and were used as received without further purification. 1-Butyl-3-methylimidazolium bromide ([BMI]Br) was prepared according to the literature method (Parnham & Morris, 2006) and was isolated as a pale-yellow oil (yield of *ca* 78%).

$AgNO_3$ (0.0687 g; 0.400 mmol), H_2atrc (0.0510 g; 0.400 mmol) and H_2Pzdc (0.0607 g; 0.361 mmol) were mixed with 0.49 g of [BMI]Br and 0.3 mL of distilled water in a *ca* 25 mL Teflon-lined stainless-steel reaction vessel. The resulting mixture was heated to 383 K for 7 days. The vessel was then allowed to cool to ambient temperature at a rate of *ca* 1 K h⁻¹. Small colourless crystals of the title compound were directly isolated from the vessel contents.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bound to carbon were placed at idealized positions with C–H = 0.95 Å, and included in the final structural model in a riding-motion approximation with the isotropic thermal displacement parameters fixed at $1.2U_{\text{eq}}$ of the carbon atom to which they are attached. Hydrogen atoms associated with nitrogen atoms were located directly from difference Fourier maps and were included in the model with the N–H and H···H (only for the –NH₂ groups) distances restrained to 0.90 (1) and 1.55 (1) Å, respectively, in order to ensure a chemically reasonable environment for these groups. These hydrogen atoms were modelled with the isotropic thermal displacement parameters fixed at $1.5U_{\text{eq}}(N)$.

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Crystal structure of 5-amino-4*H*-1,2,4-triazol-1-ium pyrazine-2-carboxylate: an unexpected salt arising from the decarboxylation of both precursors

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Computing details

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINTE-Plus* (Bruker, 2005); data reduction: *SAINTE-Plus* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

5-Amino-4*H*-1,2,4-triazol-1-ium pyrazine-2-carboxylate

Crystal data

$C_2H_5N_4^+ \cdot C_5H_3N_2O_2^-$
 $M_r = 208.19$
 Monoclinic, $P2_1/c$
 $a = 7.0599$ (5) Å
 $b = 12.1868$ (8) Å
 $c = 10.8385$ (6) Å
 $\beta = 103.593$ (4)°
 $V = 906.40$ (10) Å³
 $Z = 4$

$F(000) = 432$
 $D_x = 1.526$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1298 reflections
 $\theta = 2.6$ – 19.7 °
 $\mu = 0.12$ mm⁻¹
 $T = 296$ K
 Block, colourless
 $0.09 \times 0.04 \times 0.03$ mm

Data collection

Bruker X8 Kappa CCD APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 ω / ϕ scans
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1998)
 $T_{\min} = 0.989$, $T_{\max} = 0.997$
 12089 measured reflections

1858 independent reflections
 1037 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.077$
 $\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.6$ °
 $h = -8 \rightarrow 8$
 $k = -15 \rightarrow 15$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.133$
 $S = 1.01$
 1858 reflections
 148 parameters
 5 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.2890 (3)	0.79063 (17)	0.49872 (19)	0.0389 (6)
N2	0.0664 (3)	0.79145 (18)	0.2472 (2)	0.0468 (6)
C1	0.2177 (4)	0.8840 (2)	0.4404 (2)	0.0334 (6)
C2	0.1066 (4)	0.8815 (2)	0.3165 (2)	0.0412 (7)
H2	0.0571	0.9476	0.2797	0.049*
C3	0.1381 (4)	0.6995 (2)	0.3059 (2)	0.0448 (7)
H3	0.1147	0.6334	0.2623	0.054*
C4	0.2461 (4)	0.6993 (2)	0.4297 (3)	0.0442 (7)
H4	0.2912	0.6326	0.4668	0.053*
C5	0.2560 (4)	0.9921 (2)	0.5101 (2)	0.0378 (7)
O1	0.1745 (3)	1.07442 (14)	0.45075 (15)	0.0481 (6)
O2	0.3628 (3)	0.99415 (14)	0.61986 (16)	0.0543 (6)
N3	0.7128 (4)	0.94320 (19)	0.8957 (2)	0.0622 (8)
N4	0.6167 (4)	0.88117 (19)	0.7929 (2)	0.0476 (6)
H4A	0.535 (3)	0.912 (2)	0.7253 (18)	0.071*
N5	0.7480 (3)	0.76575 (18)	0.93596 (19)	0.0417 (6)
H5	0.778 (4)	0.6996 (13)	0.972 (2)	0.063*
N6	0.5628 (4)	0.6942 (2)	0.7405 (2)	0.0540 (7)
H6A	0.473 (3)	0.714 (2)	0.6709 (19)	0.081*
H6B	0.585 (5)	0.6271 (13)	0.775 (3)	0.081*
C6	0.6369 (4)	0.7751 (2)	0.8181 (2)	0.0365 (7)
C7	0.7892 (5)	0.8695 (2)	0.9782 (3)	0.0553 (8)
H7	0.8649	0.8861	1.0584	0.066*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0450 (14)	0.0290 (13)	0.0400 (12)	−0.0006 (11)	0.0049 (10)	0.0005 (10)
N2	0.0557 (16)	0.0387 (14)	0.0406 (12)	0.0008 (12)	0.0005 (11)	−0.0086 (12)
C1	0.0331 (15)	0.0309 (15)	0.0355 (13)	−0.0004 (13)	0.0067 (11)	0.0022 (12)
C2	0.0495 (18)	0.0320 (16)	0.0367 (14)	0.0061 (14)	−0.0007 (13)	0.0020 (12)
C3	0.0487 (19)	0.0352 (17)	0.0478 (16)	−0.0016 (15)	0.0059 (14)	−0.0099 (13)
C4	0.0499 (18)	0.0299 (16)	0.0497 (16)	0.0036 (14)	0.0056 (14)	0.0028 (13)
C5	0.0420 (17)	0.0344 (16)	0.0330 (13)	0.0001 (14)	0.0006 (12)	0.0036 (12)
O1	0.0625 (14)	0.0319 (11)	0.0402 (10)	0.0058 (9)	−0.0074 (9)	0.0021 (8)
O2	0.0708 (14)	0.0375 (12)	0.0399 (10)	0.0067 (10)	−0.0165 (10)	−0.0025 (9)
N3	0.089 (2)	0.0419 (15)	0.0461 (14)	0.0029 (15)	−0.0032 (13)	0.0024 (12)
N4	0.0625 (18)	0.0367 (15)	0.0386 (13)	0.0037 (13)	0.0019 (12)	0.0061 (11)
N5	0.0480 (14)	0.0362 (15)	0.0359 (12)	0.0025 (12)	−0.0004 (11)	0.0083 (11)

N6	0.0607 (18)	0.0440 (16)	0.0491 (15)	-0.0005 (15)	-0.0038 (13)	0.0030 (13)
C6	0.0391 (17)	0.0349 (18)	0.0348 (13)	0.0044 (13)	0.0068 (12)	0.0057 (12)
C7	0.074 (2)	0.046 (2)	0.0383 (15)	0.0020 (17)	-0.0026 (15)	0.0012 (14)

Geometric parameters (Å, °)

N1—C4	1.335 (3)	N3—C7	1.293 (3)
N1—C1	1.341 (3)	N3—N4	1.384 (3)
N2—C2	1.323 (3)	N4—C6	1.322 (3)
N2—C3	1.328 (3)	N4—H4A	0.902 (10)
C1—C2	1.387 (3)	N5—C6	1.338 (3)
C1—C5	1.512 (3)	N5—C7	1.353 (3)
C2—H2	0.9300	N5—H5	0.901 (10)
C3—C4	1.379 (4)	N6—C6	1.321 (3)
C3—H3	0.9300	N6—H6A	0.899 (10)
C4—H4	0.9300	N6—H6B	0.896 (10)
C5—O2	1.250 (2)	C7—H7	0.9300
C5—O1	1.256 (3)		
C4—N1—C1	115.6 (2)	C7—N3—N4	102.9 (2)
C2—N2—C3	114.9 (2)	C6—N4—N3	111.1 (2)
N1—C1—C2	120.2 (2)	C6—N4—H4A	126 (2)
N1—C1—C5	120.1 (2)	N3—N4—H4A	121.7 (19)
C2—C1—C5	119.8 (2)	C6—N5—C7	105.9 (2)
N2—C2—C1	124.4 (2)	C6—N5—H5	121.3 (18)
N2—C2—H2	117.8	C7—N5—H5	132.7 (18)
C1—C2—H2	117.8	C6—N6—H6A	115 (2)
N2—C3—C4	122.0 (2)	C6—N6—H6B	115 (2)
N2—C3—H3	119.0	H6A—N6—H6B	128 (3)
C4—C3—H3	119.0	N6—C6—N4	126.2 (2)
N1—C4—C3	123.0 (2)	N6—C6—N5	126.9 (2)
N1—C4—H4	118.5	N4—C6—N5	106.9 (2)
C3—C4—H4	118.5	N3—C7—N5	113.2 (2)
O2—C5—O1	125.0 (2)	N3—C7—H7	123.4
O2—C5—C1	119.3 (2)	N5—C7—H7	123.4
O1—C5—C1	115.7 (2)		
C4—N1—C1—C2	0.3 (4)	N1—C1—C5—O1	-176.1 (2)
C4—N1—C1—C5	179.5 (2)	C2—C1—C5—O1	3.1 (4)
C3—N2—C2—C1	1.2 (4)	C7—N3—N4—C6	0.8 (3)
N1—C1—C2—N2	-1.4 (4)	N3—N4—C6—N6	179.8 (3)
C5—C1—C2—N2	179.4 (2)	N3—N4—C6—N5	-0.9 (3)
C2—N2—C3—C4	-0.1 (4)	C7—N5—C6—N6	179.9 (3)
C1—N1—C4—C3	0.8 (4)	C7—N5—C6—N4	0.6 (3)
N2—C3—C4—N1	-1.0 (4)	N4—N3—C7—N5	-0.4 (4)
N1—C1—C5—O2	3.7 (4)	C6—N5—C7—N3	-0.1 (4)
C2—C1—C5—O2	-177.1 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N4—H4A \cdots O2	0.90 (1)	1.77 (1)	2.655 (3)	166 (3)
N5—H5 \cdots O1 ⁱ	0.90 (1)	1.73 (1)	2.632 (3)	176 (3)
N6—H6B \cdots O2 ⁱ	0.90 (1)	1.97 (1)	2.853 (3)	169 (3)
N6—H6A \cdots N1	0.90 (1)	2.21 (1)	3.099 (3)	169 (3)

Symmetry code: (i) $-x+1, y-1/2, -z+3/2$.